N O T I C E

HSR Division | Date : July 02, 2002 | Notice No 0093

Time Sensitive, Shock Sensitive, Peroxide Forming Chemical Management and Compatible Storage

Overview

The publication of this Notice rescinds Attachment 5 of the Chemical Management LIR 402-510-01.0. The last sentence in Section 5.1.7 of the LIR, "Since peroxide forming and shock sensitive compounds have a limited shelf life (Attachment 5), the safety-and-environmentally-responsible line manager shall determine a disposal plan for items having a short shelf-life;" is also rescinded. This Notice shall replace Attachment 5. This Notice covers requirements that shall be implemented for labeling, testing and storing time sensitive, and peroxide forming chemicals; inspecting, using, and storing shock sensitive, explosive when dry, and explosive chemicals; and segregating incompatible chemicals.

Chemical owners shall manage peroxide forming and explosive when dry chemicals according to this Notice. Labeling and management of chemicals shall be the responsibility of chemical owners. The group safety-and-environmentally-responsible line manager shall have two months from the publication of this Notice to ensure labeling, examination, or disposal of the time sensitive, shock sensitive, and peroxide forming chemicals that meet or exceed the shelf-life. HSR-5 shall send a list of active chemical containers and labels to each group to facilitate completion of this process.

The significant changes presented in this Notice that shall be implemented are:

- A maximum time storage limit for peroxide forming chemicals.
- Additional chemicals added to the peroxide forming list.
- Addition of polynitro and nitrato compound list.
- Addition of DOT Forbidden list.
- Addition of no disposal path list.
- Stabilization allowed only after a review of the procedure.
- Detonation no longer used for mitigation of explosion hazard.
- Annual inspection of explosive when dry chemicals changed to quarterly inspection.
- Additions made to the Compatibility Table.
- Reactive Chemistry training availability.

Background

In 2001, ESH Division with the help of an expert subcontractor examined peroxide forming materials at LANL and determined that LANL retention of shock sensitive and peroxide forming chemicals needed clarification and risk reduction improvement. Chemicals showing peroxide test results greater than 100 ppm were: Dioxane, THF, Dimethoxymethane, Propyl ether, 2-butanone, Sec-butanol, Ethylene glycol dimethyl ether, and 2-butoxyethanol. Some of the THF containers were less than 4 months old. Refrigeration did not prove to be a mechanism to inhibit peroxide formation and could actually increase peroxide formation. The ability of a reactive chemical to have increased peroxide levels was dependent upon exposure to air, rapid temperature changes, UV light, or metal catalysts. Inhibitors were consumed over time.

Additionally, several nitrato chemicals were discovered in a dry, crystalline state which had a potential for explosion if mishandled. The following areas were identified for clarification:1) Determine the maximum shelf-life for peroxide forming chemicals; when the maximum shelf-life has been reached the container shall be disposed if safe; 2) Develop a reference list of peroxide formers, explosive when dry, and DOT Forbidden chemicals; and 3) Develop safe handling practices.

Requirements

Procurement

- Purchases shall be limited to the quantity that can be used before shelf-life is reached.
- The disposal path shall be determined before purchasing a chemical. DOT Forbidden materials shall not be offered or accepted for disposal or transportation unless the material is diluted, stabilized, or incorporated into a device. (Specifics can be found in DOT Forbidden Table at http://eshdb.lanl.gov/~esh5/cma/index.html and 49 CFR 173.21 and 173.54.)
- The chemical owner and the supervisor shall ensure that facilities are authorized for explosives work and that personnel receiving explosive materials are authorized and trained for work with peroxide forming chemicals, polynitro and nitrato compounds, and DOT forbidden materials.
- The chemical owner and safety-and-environmental-responsible-line-manager shall ensure that the Explosives Review Committee (ERC) reviews and approves any explosive (1) to be introduced into the Laboratory for the first time, (2) to be used in an unusual manner, or (3) to be used by a group not normally involved in work with explosives. See Explosives LIR 402-550-01.0 *Click here* for additional procurement review and transportation requirements.
- An approved HCP detailing experimental boundaries shall be required for work with peroxide formers, shock sensitive, polynitro and nitrato compounds, and DOT forbidden chemicals.

Upon Receipt

- For operations areas that have not been approved/authorized for explosive operations, the ERC must approve any operations for work with DOT Forbidden materials (see http://eshdb.lanl.gov/~esh5/cma/index.html)
- Containers must be checked to ensure that the cap and container have not been damaged during transport or if an obvious loss of material occurred.
- The date received and required disposal date must be recorded on a label or other visible means of documentation, i.e. clipboard, posted tag, etc., on all original and secondary containers. (see labels in Figure 1. Templates available at http://eshdb.lanl.gov/~esh5/cma/index.html) The date received; required disposal date; and testing/inspection labels and signal warning stickers must accompany any secondary containers dispensed from the original container.
- The MSDS must be read and the manufacturer's storage segregation guidelines followed. **Guidance Note**: If a substance forms explosive peroxides or polymerizes rapidly, there will be a warning under the heading *Precautionary Labeling or Fire and Explosion Hazard Data* on the MSDS.
- For peroxide forming chemicals, the contents must be tested with peroxide test strips when they arrive at location of use

and before each use. Each test result must be documented on a label (See labels in Figure 1. Templates available at http://eshdb.lanl.gov/~esh5/cma/index.html) or other visible documentation method. 30 PPM shall be the maximum allowable peroxide level. Follow requirements under "Each Use."

- For air reactive, explosives when dry, and DOT Forbidden compounds; required solvation shall be maintained. Containers shall be stored in a segregated and cool dark place.

Each Use

- The cap, container and contents shall be checked for deterioration.
- For original and secondary containers of peroxide forming chemicals, the contents shall be tested with peroxide test strips before each use. Document each test result on a label (See labels at http://eshdb.lanl.gov/~esh5/cma/index.html) or other visible documentation method. When a pattern of increasing peroxide test results up to 30 PPM are identified, additional inhibitor shall be added to maintain usability or the chemical shall be disposed. If the material is intended for discard, it shall be managed as waste pursuant to applicable requirements (contact SWRC at MS K490, 7-0666). When the quantitative levels of peroxide approach 30 PPM or when the dispose date in the Tables at http://eshdb.lanl.gov/~esh5/cma/index.html is reached (which ever comes first) the chemical must be disposed. 30 PPM shall be the maximum allowable peroxide level.
- Inert gas blankets must be introduced before closing the cap each time the peroxide container is opened. Heat and light exposure must be avoided. **Exception:** vinyl monomers which need oxygen for inhibitors to work properly.

Disposal

- Maximum shelf-life shall be in accordance with the criteria contained in tables at http://eshdb.lanl.gov/~esh5/cma/index.html
- Enough time in advance of the terminal disposal date shall be allowed to complete disposal paperwork and pickup.
- Residual chemicals must not be bulked-up.
- Reactive nitro, chlorate, and perchlorate compounds that are known to react with organic and inorganic contaminants to form highly sensitive and powerfully explosive salts (e.g., picric acid, styphnic acid and their salts with metal contaminants) shall be used or disposed of in five years.

Exceptions

- Unopened ampules stored in dark, inert atmosphere shall be kept no longer than 5 years before they are disposed if there is no visible discoloration or other change in appearance prior to that time. The unopened ampules shall be inspected annually and the inspection date shall be documented in the institutional Chemical Inventory System by entering a new inventory date.
- Solvents that are to be stored in an inert-atmosphere glovebox for their entire shelf-life shall be exempt from the three-month disposal limit so long as the inert atmosphere of the glovebox is maintained. The atmosphere must be verified by a continuous reading oxygen meter or by weekly indicator (spot) tests to contain less than 10 ppm oxygen at all times. The chemicals must be tested every three months for peroxide

content, and immediately disposed if peroxide content equals 30 ppm. If the peroxide level exceeds 30 ppm, stabilization must occur before disposal. Call 7-2854 for assistance. If the glovebox atmosphere is compromised (i.e., the oxygen level in the box exceeds 1000 ppm or 0.1%), the peroxide forming chemicals shall be tested immediately and disposed if the peroxide content equals 30 ppm.

Stabilization

Proposed stabilization shall require a review of the procedure or accomplished in conjunction with a subcontractor technical expert. Proposed stabilization procedures must be submitted to HSR-5 for review at MS K499. Contact 7-2854 for assistance. Stabilization shall occur in a hazardous waste <90 day storage area pursuant to hazardous waste requirements. To establish a <90 day storage area and address other requirements for treatment such as locations, SWRC shall be contacted at MS K490, 7-0666.

Training

It is recommended that chemical owners and users of peroxide forming, explosive when dry, polynitro and nitrato compounds, and DOT forbidden materials complete Reactive Chemistry training which will be provided through a subcontractor technical expert based on demand.

Quarterly Inspections

- Polynitro and nitrato chemicals and DOT Forbidden chemicals http://eshdb.lanl.gov/~esh5/cma/index.html shall be inspected quarterly to assure required solvation. The integrity of the container, cap, and contents must be checked and the inspection dates shall be documented in the institutional Chemical Inventory System by entering a new inventory date.
- Polynitro compounds shall be kept wet (with water or solvent) where advised by the manufacturer.
- Nitro compounds requiring amine stabilizers (e.g., 2° nitrate esters such as nitroglycerine or butane triol trinitrate stabilized with n-methyl-p-nitroaniline or 2-nitrodiphynylamine), must be checked for stabilizer content at least annually and stabilizer added as required.
- Any peroxide forming chemical with visible discoloration, crystallization, change in viscosity or liquid stratification shall be treated as potentially explosive. Other visual indicators of a hazard situation include a missing or loose lid and the reduction of liquid level to less than 10% of original volume with a large amount of air above the liquid. **The cap SHALL NOT be removed. The container SHALL NOT be moved. The cabinet or lab space SHALL BE locked out.** Chemical Management Support at 7-2854 or the ERC Chair at 7-5653 shall be contacted for visual inspection and technical support.
- Any shock sensitive, polynitro and nitrato chemical with visible discoloration or other change in appearance shall be treated as an explosive. **The cap SHALL NOT be removed. The container SHALL NOT be moved. The cabinet or lab space SHALL BE locked out. .** Chemical Management Support at 7-2854 or the ERC Chair at 7-5653 shall be contacted for visual inspection and technical support.
- Potassium, sodium, cesium, etc. and other air reactive chemicals shall be stored under kerosene or oil. These chemicals must be inspected to ensure they are still completely covered and the inspection date shall be documented in the institutional Chemical Inventory System.

Additional Precautions:

- Peroxide formers of an unknown age or unknown use history must not be opened. The ERC Chair at 7-5653 or Chemical Management Support at 7-2854 must be contacted for assistance.
- Butadiene, Chloroprene, Divinyl acetylene, Isopropyl ether, Tetrafluorethylene, and Vinylidene chloride may spontaneously form peroxides that will make the materials shock or heat sensitive "on the shelf", that is, without any further concentration through evaporation or distallation. The 3-month storage limit shall be strictly enforced. Store under nitrogen, if practical.
- Potential peroxide forming chemicals must never be distilled to dryness. A minimum of 20% still bottoms must always be left. Adding a non-volatile organic compound (such as mineral oil) can dilute the peroxides remaining after distillation.
- Glassware or containers that have been used with peroxide forming compounds must never be scrubbed or scraped if an oily or crusty residue is observed.

Storage

- Storage cabinets must not be overloaded. Enough space shall be ensured between chemical containers so that a visual inspection can be conducted without moving multiple containers.
- Corrosion-resistant storage trays or secondary containers shall be used to retain materials if the original container breaks or leaks.

- **Compatibility**

A chemical compatibility chart that shall be used for determining a segregation plan is available at URL http://eshdb.lanl.gov/~esh5/cma/index.html.

Guidance Note: The following web sites may be useful:
The US Coast Guard Cargo Compatibility Chart can be found at http://tis.eh.doe.gov/web/chem_safety/Docs/compat.pdf .
The University of Nebraska-Lincoln Compatibility Chart of Chemical Mixtures can be found at http://bifrost.unl.edu/ehs/ChemicalInfo/comptabl.html

References

NFPA (National Fire Protection Association), "Fire Protection for Laboratories Using Chemicals," Standard No. 45, most recent edition, Quincy, Massachusetts.
NFPA (National Fire Protection Association), "Standard for the Storage, Use and Handling of Compressed and Liquefied Gases in Portable Cylinders," Standard No. 55, most recent edition, Quincy, Massachusetts.
SafetyNet #23 Peroxide Formation in Chemicals, UC Davis Environmental Health and Safety.

Questions?

Technical assistance and/or questions shall be directed to Helena Whyte (HSR-5), 7-2854 or e-mail acis@lanl.gov.

The OIC for this Notice is HSR-5, Industrial Hygiene and Safety; and the responsible division director is the HSR-DO. This Notice shall remain in effect until LIR 402-510-01.0 has been revised.

Los Alamos NATIONAL LABORATORY

Figure 1 Testing/Inspection Documentation (These labels or some other form of visible documentation are mandatory.)
(Use Labsafety 3"X5" label, order number 9L-68253)
Formatted templates are available at http://eshdb.lanl.gov/~esh5/cma/index.html

Peroxidizable Chemical Label

Peroxidizable Compound
May Become Explosive with Time or Exposure to Air or Light

Date Received:_____ Date Opened:_____
Chemical Owner:_____
Test Each Use After Opening

Test Date:	Results PPM	Initial
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

Discard Chemical if Results are 30 ppm; or if chemical is ☐3mo ☐6mo ☐12mo (check appropriate time). See URL http://eshdb.lanl.gov/~esh5/cma/index.html for lists.

WARNING: If a viscous liquid or crystalline solid is found in the material, do not open or attempt to move the container! Take Special care to check around the cap. If already opened, do not re-tape.

Contact ESH POC with any questions

Time Sensitive Chemical Label

May Become Explosive with Time or Exposure to Air or Light

Date Received:_____ Date Opened:_____
Chemical Owner:_____
Check Each Use or quarterly After Opening

Date Checked:	Status	Initials
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

WARNING: If a viscous liquid or crystalline solid is found in the material, do not open or attempt to move the container! Take Special care to check around the cap. If already opened, do not re-tape.

Contact ESH POC with any question

Warning: Explosive when Dry

Store well away from sources of vibration.
Store in cool, temperature-controlled areas (avoid sunlight).
Keep solvated (unless approved by the Explosives Review Committee).

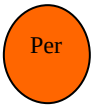
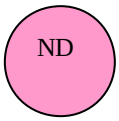
INSPECTION RECORD

Date_____ Inspected by_____

Date_____ Inspected by_____

Date_____ Inspected by_____

Attachment 1
Non Mandatory Best Practice Signal Word Labeling

Labels (use Avery label# 5293) Available from HSR-5 or http://eshdb.lanl.gov/~esh5/cma/index.html)	**Definition**	**When to use.**
	Peroxide Forming Material	All known peroxide forming compounds (original containers and secondary containers dispensed from the original container) shall be conspicuously labeled with this signal warning sticker. See the peroxide lists at URL http://eshdb.lanl.gov/~esh5/cma/index.html They must be tested before each use. They shall be disposed when the peroxide level approaches 30 ppm or when the dispose date in the tables has been reached, whichever is sooner. Stabilization shall only be allowed with approved procedure. (Submit to HSR-5 for review, MS K499 or call 7-2854 for assistance.)
	Explosive when dry	All known explosives when dry compounds (original containers and secondary containers dispensed from the original container) shall be conspicuously labeled with this signal warning sticker. (See the polynitro and nitrato list at URL http://eshdb.lanl.gov/~esh5/cma/index.html). These containers shall be checked quarterly to ensure that they remain wet. (Call the ERC or HSR-5, 7-2854 if the containers are considered to be unstable.)
	DOT Forbidden	All known DOT forbidden compounds (original containers and secondary containers dispensed from the original container) shall be conspicuously labeled with this signal warning sticker. (See the DOT forbidden table at URL http://eshdb.lanl.gov/~esh5/cma/index.html). DOT Forbidden materials shall not be offered or accepted for disposal or transportation unless the material is diluted, stabilized, or incorporated into a device. (Specifics can be found in DOT Forbidden Table and 49 CFR 173.21 and 173.54.) They must be inspected for discoloration and required solvation quarterly. The Explosive Review Committee (ERC) must approve any operations for work with DOT Forbidden materials before use.
	No Disposal Path	All chemicals with “no disposal path” (original containers and secondary containers dispensed from the original container) shall be conspicuously labeled with this signal warning sticker. (See the No Disposal Path list at URL http://eshdb.lanl.gov/~esh5/cma/index.html). A substitute chemical shall be acquired rather than the purchase of a No Disposal Path chemical.